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Determination of Trace Metals in Effluents by Differential Pulse Anodic Stripping Voltametry

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16 ABSTRACT

Differential pulse anodic stripping voltametry (DPASV) was evaluated to determine its applicability to industrial and domestic effluents. The results show that trace amounts of zinc, cadmium, lead, bismuth, copper, thallium, indium, antimony, tin and nickel can be determined individually and simultaneously. A procedure for providing low blank buffer and electrolyte systems was tested. The efficiency for the entire process, including digestion, sample transfer and analysis, was found to range from 93 to 100%. Pulse anodic stripping voltametry was found to be superior to atomic absorption in terms of sensitivity, detection limits and cost.

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DETERMINATION OF TRACE METALS IN EFFLUENTS BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water; conduct studies to determine the response of aquatic organisms to water quality.

- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in the use of instrumental methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordingly, the Environmental Monitoring and Support Laboratory has an on-going methods research effort in the development, evaluation, and modification of instrumental methods. This particular report pertains to the evaluation of differential pulse anodic stripping voltametry. The method has potential routine application for the analysis of trace metals in surface waters and domestic and industrial wastes.

Dwight G. Ballinger, Director
Environmental Monitoring & Support Laboratory
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ABSTRACT

This investigation was designed to appraise the applicability of differential pulse anodic stripping voltammetry to the determination of trace metals in a wide variety of industrial and domestic effluents. Fifteen (15) types of effluents of different industrial processings were employed, providing a rather comprehensive matrix base for assessing the potential for practical utilization of the technique.

The results revealed that the technique is highly sensitive and that practical application to total metal determination requires careful analytical work and a quality of sample digestion with which present state-of-the-art digestion procedures cannot comply. However, when the technique is coupled with a closed-system acid digestion process, zinc, cadmium, lead, nickel, antimony, bismuth, copper, thallium, tin and indium can be determined individually and simultaneously in groups at concentrations ranging from the sub-parts-per-billion to the parts-per-million levels. A procedure for providing low blank buffer and electrolyte systems was tested, and the efficiency for the entire process, including digestion, sample transfer and analysis, was found to range from 95 to 100%.

Quantitative data for samples of complex matrices were in good agreement with flame atomic absorption spectrophotometric results for each element investigated.

From 40 to 50 previously digested samples with 4 to 5 elements per sample can be analyzed each 8 hour working day (corresponding to 160 to 250 individual determinations) at about one-third the costs for flame atomic absorption spectrophotometry.

This report was submitted in fulfillment of Grant Number R803400-01-0 by Benedict College, Columbia, South Carolina, under the sponsorship of the U. S Environmental Protection Agency. Work was completed as of February 1, 1977.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Acknowledgment viii

I. Introduction 1
II. Conclusions 3
III. Recommendations 4
IV. Development of Digestion Procedures 5
V. Evaluation of Reagent Purification Procedures 7
VI. Development of Qualitative and Quantitative Methods . 10
VII. Evaluation and Application of Analytical Methods . . 21
VIII. Comparison of Differential Pulse Anodic Stripping Voltammetry and Flame Atomic Absorption Spectrophotometry for Effluent Analysis . . 26
IX. Discussion 31

References

FIGURES

Number		Page
1	Current-potential curves for DPASV in purified and unpurified sodium acetate	9
2	Reproducibility of DPASV for simultaneous stripping of zinc, cadmium, lead and copper in 0.5 F sodium fluoride	19
3	Peak current versus concentration for the simultaneous stripping of Zn, Cd, Pb, Bi and Cu	20
4	Atomic absorption calibration curves for tin, zinc, and bismuth	26
5.	Atomic absorption calibration curves for cadmium and lead	27
6	Dependency of reduction potential on atomic radius	33
7.	Separation of copper and bismuth signals for DPASV using acetate ion	35
8	Current-potential curves for the simultaneous stripping of Cd, Pb, Cu and Bi in the presence of ammonia and carbonate	38

TABLES

Number		Page
1	Trace Metal Contamination in Different Batches of Recrystallized Sodium Acetate	8
2	Types of Effluents and the Number of Samples Analyzed Through this Study	18
3	Trace Metals in a Mixture of Industrial Effluents and Precision Data	23
4	Recovery Data for the Simultaneous Determination of Zinc, Cadmium and Lead in Industrial Mixture II	23
5	Results from Application of DPASV to a Variety of Effluents	24
6	Comparison of DPASV and Flame AAS Data for Metals in Effluents	28
7	Comparison of Sensitivities, Detection Limits and Linearity Range of Trace Metal Determination for DPASV and Flame AAS	28
8	Comparison of Start-up Costs for DPASV and Flame AAS	29
9	Advantages and Disadvantages of DPASV and Flame AAS	30
10	Correlation between Reduction Potentials and Electronic Configurations of Metal Ions	32

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SECTION 1

INTRODUCTION

This investigation comprised an appraisal of the applicability of differential pulse anodic stripping voltametry (DPASV), using the hanging mercury drop electrode, to the identification and determination of trace metals in a wide variety of industrial and domestic effluents. Its scope also encompassed the development and evaluation of sample pretreatment and reagent purification procedures to be used in conjunction with a highly sensitive technique. Problems associated with day-to-day individual determination of zinc, cadmium, lead, copper, bismuth, thallium, tin, indium, nickel and antimony were developed.

Since flame atomic absorption spectrophotometry (AAS) is the most widely used technique for routine determination of metals in water and wastewaters, a phase of this research constituted a comparative study of AAS and DPASV for analysis of effluents. Advantages and disadvantages of both techniques were explored, and cost data based on present-day economics were generated.

This report then, is not just a compilation of data to demonstrate the technical elegance of DPASV, but is a prescription for its application to routine analysis of effluents with complex matrices and ranging from domestic to that of the metals plating industry.

Experimentation proceeded in several phases. The first phase involved (a) development of sample digestion procedures; (b) evaluation of reagent purification procedures; and (c) development of methods for identification of metals. Phase two constituted: (a) development of methods for the quantitative determination of metals and (b) application of these methods to the analysis of effluents. In phase three, a comparative study of flame AAS and DPASV was conducted for determining metals in the same set of effluent samples. Advantages and disadvantages of both techniques were assessed.

Several questions surfaced prior to the commencement of this study and, perhaps, are expressive of the scientific curiosity that gave birth to it. These are: What metals can be identified and determined by DPASV and at what levels of detection; can a generalized procedure be given for all possible metals or groups of these metals in all types of effluent samples; and, what advantages and disadvantages exist for total metal determination? Each phase of this investigation was designed to, in some

way, provide an answer to each of the above questions.

The basic principle of anodic stripping voltametry has been well presented by Barendrecht (1). It is basically a two-step process that involves a preconcentration phase and a stripping phase. Preconcentration is achieved by cathodically reducing the metal ion(s) of interest at a constant potential that is 300 or 400 millivolts more negative than the polarographic half-wave potential, $E_{1/2}$, of the ion of interest or of the ion with the most negative $E_{1/2}$ value. The solution is usually agitated or the electrode is rotated during this first phase. Following preconcentration a rest period of about 20 to 30 seconds is allowed for quiescent conditions to develop. Anodic stripping is then initiated by applying a potential that is a linear function of time. In brief, this excitation function consists of a fixed-height potential pulse occurring at regular intervals and superimposed on a slowly varying linear potential ramp.

Characteristics of the current-potential signal such as the peak current (i_p) and the half-peak potential ($E_{p/2}$) were tested for their analytical utility in effluents. Theoretically, i_p is a linear function of the cell concentration and $E_{p/2}$ is characteristic of the metal being oxidized. Values for these parameters for a metal depend upon the properties of a particular electrolyte system --such as its pH, ionic strength and complexing capability --and on the electrode system. The indicator electrode used throughout this study was a hanging mercury drop electrode (HMDE).

The experimentally controllable parameters are rate of stirring, mercury drop size, preconcentration time (t_d), preconcentration potential (E_d), scan rate (v), the solution volume and the temperature.

SECTION II

CONCLUSIONS

It is concluded from this study that trace amounts of zinc, cadmium, lead, bismuth, copper, thallium, tin, indium, antimony and nickel can be identified and determined in industrial and domestic effluents by DP/ASV following digestion in a closed system. This system and technique, with regard to total metal determination, is highly competitive with AAS in terms of precision and accuracy, and is superior to AAS in terms of sensitivity, detection limits and costs. Although the process requires sample pretreatment, it is a non-destructive technique, and qualitative and quantitative analyses can be carried out on a sample simultaneously for as many as five elements.

SECTION III

RECOMMENDATIONS

The investigator recommends that:

1. ICP/AES with the closed acid digestion system be employed as an alternative method to AAS for routine quantitative determination of total trace metals such as zinc, cadmium, lead, bismuth, copper, thallium, tin and indium in industrial and domestic effluents;

2. This technique and system be employed as the most feasible method for the simultaneous identification of these metals at trace and ultratrace levels in effluents; and

4. The Chelex-100 ion exchange technique be employed as the most feasible procedure for rapid removal of trace metals from electrolyte systems.

SECTION IV

DEVELOPMENT OF DIGESTION PROCEDURE

A number of digestion procedures involving wet and dry ashing were explored and found to be inadequate for the sensitive technique of DPASV. Trace amounts of organic material and potential complexing species were found to have a pronounced effect on the position ($E_{p/2}$) and size (i_p or q, the number of coulombs) of the current potential signal for a particular metal. Continuous boiling of samples in an oxidizing acid system may have been adequate for destroying the organic material, but led to considerable metal contamination and loss of volatile metal constituents.

This evidence dictated the need for a non-contaminating, closed digestion system that could be subjected to high temperatures when charged with a concentrated oxidizing acid solution.

The Parr Acid Digestion Bomb, Model No. 4745 (Parr Instrument Co., Moline, Illinois) appeared to be a prime candidate. It consisted of a Teflon (Trademark of E. I. Dupont Co., Delaware) cup and cover and a stainless steel encasement with a spring-loaded closure and screw cap. This general purpose bomb withstood temperatures up to 150°C and pressures up to 1000 psig. The furnace used to perform digestions was a Lab Heat Muffle Furnace (Blue M Electric Co., Blue Island, Illinois).

Procedures that were developed for the digestion of industrial and domestic effluents using the Parr Acid Digestion Bomb are given below:

(1) Weigh to the nearest 0.1 mg a previously leached and rinsed Teflon cup. (This step may be omitted if the sample does not contain a high percentage of particulates and the concentration can be more appropriately expressed as weight of analyte/volume of effluent);

(2) Pipet from 0.050 to 10.0 ml of the thoroughly mixed sample into the Teflon cup (The sample size will depend upon the expected level of analyte in the sample);

(3) Weigh Teflon cup with sample to the nearest 0.1 mg (This step may be omitted if step #1 is omitted);

4. Add 0.5 to 3 ml of high purity nitric acid to the Teflon cup (if the total volume of liquid in the Teflon cup is less than 3 ml add enough distilled-deionized water to bring the final volume to approximately 3 ml);

5. Place Teflon cup in the encasement and tighten screw cap by hand;

6. Place bomb in a furnace that has been preheated to 150°C;

7. Allow time for thermal equilibrium to be attained and adjust the temperature to 165°C;

8. Heat from 1 to 8 hours or more (depending upon the complexity of the sample matrix) at 165±5°C;

9. Allow bomb to cool and transfer sample to a volumetric flask (10, 25, or 50 ml capacity). Dilute to the mark with the appropriate buffer system for determining the analyte of interest (see SECTION VI - DEVELOPMENT OF QUALITATIVE AND QUANTITATIVE METHODS).

SECTION V

EVALUATION OF BEAKER VERIFICATION TESTING

The technique of DPASV has the capability of detecting a number of metals at the nanogram/ml and subnanogram/ml levels. To exploit this capability required the use of electrolytes and buffer systems of high purity and quality. Reagent grade chemicals contained high levels of impurities (see Curve B of Figure 1) and were not suitable for methods using DPASV for analytical measurements. High purity versions of most of these reagents were not available through the market and/or were highly expensive. For cells, repeated recrystallization was attempted but was found to be laborious and, in most cases, inadequate (see Table 1).

Electrolytic purification was found to be adequate but required the use of a potentiostat and a purification period of 24 hours per liter of electrolyte.

A procedure employing the cation form of Chelex 100 (100 - 200 mesh) ion exchange resin (Bio-Rad Laboratories, Richmond, California) was evaluated and found to be suitable. The material is an ion exchange resin that has the capability of removing copper, lead, zinc and other heavy metals from aqueous solutions. Curve A in Figure 1 reveals its effectiveness in removing contaminants from a 1M sodium acetate solution after just one pass through a column. Two passes gave a blank solution with virtually no detectable amounts of metal contaminants.

TABLE 1. TRACE METAL CONTAMINATION IN DIFFERENT BATCHES OF RECRYSTALLIZED SODIUM ACETATE

Batch no.	Metal concentration (ng/ml)*			
	Zinc	Cadmium	Lead	Copper
1	148	5.00	80.5	80.4
2	100	3.12	40.2	37.8
3	70.0	2.30	46.8	61.5
4	17.0	2.50	40.0	81.8

* Concentration values are for 2 M sodium acetate solutions prepared from different batches of recrystallized sodium acetate.

The following procedures for preparing, using and regenerating the column gave good results in our laboratory:

1. Prepare approximately 50 ml of a saturated solution of disodium or tetrasodium ethylenediaminetetraacetate.

2. Warm on a hot plate and added enough Chelex 100 (Na+ form, 100 to 200 mesh).

3. Develop column (A 50 ml buret with a plug of glass wool near the outlet will be adequate).

4. Wash extensively with distilled - deionized water (about 10 bed volumes).

5. Adjust the pH of the solution of interest to a value above 7.

6. Pass solution through column twice. A flow rate of about 4 ml/min/cm^2 is adequate. To regenerate the column pass through 2 bed volumes of high purity IF HNO_3, 6 bed volumes of distilled-deionized water, 2 bed volumes of 1F NaOH, and 6 bed volumes of water.

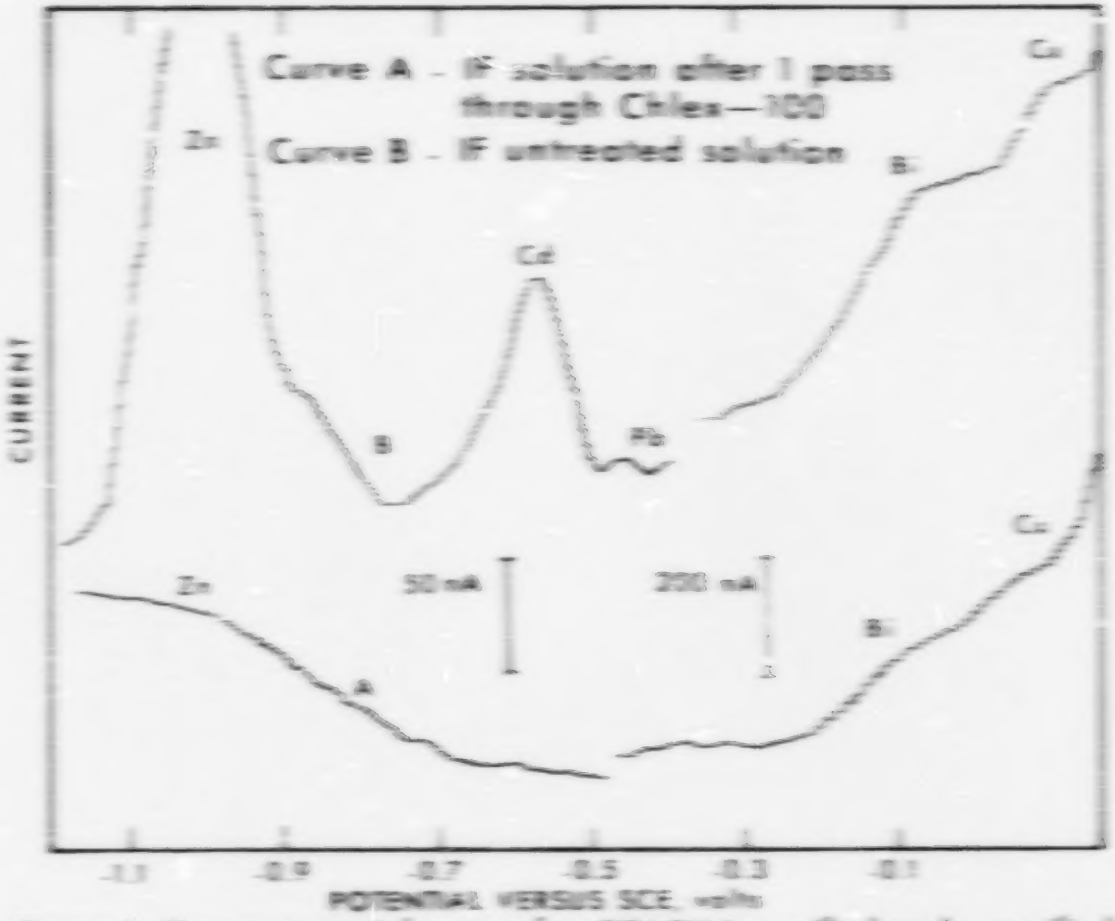


Figure 1. Current potential curves for DPASV in purified and unpurified sodium acetate.

SECTION VI

DEVELOPMENT OF QUALITATIVE AND QUANTITATIVE METHODS

The anodic stripping data were generated by use of a Model 174 Polarographic Analyzer (Princeton Applied Research Corporation, Princeton, New Jersey) that was connected to a Model [illegible] Omnigraphic X - Y Recorder (Houston Instruments, Houston, Texas). This instrument was operated in the differential pulse mode and the current output was always in the microampere range.

The electrochemical cell consisted of a glass bottom and a self-mounting plastic top that was purchased from Princeton Applied Research Corporation. The reference electrode was a saturated calomel electrode (SCE) with a salt bridge attached. A piece of pyrex Vycor (Corning Glass) silicated glass, attached at the end of the isolated electrode tube and held in place by a Teflon (Dupont) sheath, served as the salt bridge tube between the isolated electrode and the solution in the electrolysis cell. This cavity was filled with the same electrolyte system that was used for the test solution. A spiral of platinum wire served as the isolated electrode. The sparge tube consisted of a two-way Teflon stopcock, a glass tube and a tapered Teflon tip (Princeton Applied Research Corporation).

The sparge tube was connected to a train assembly that consisted of a wash bottle containing a concentrated disodium ethylenediaminetetraacetate solution, a wash bottle containing a vanadous chloride solution and a tank of high purity nitrogen gas. Vanadous chloride solution served as an oxygen scrubber while the disodium EDTA served to remove trace metals from the gas stream.

Ultrex grade nitric acid (J. T. Baker Company, Phillipsburg, New Jersey), high purity metals and demineralized - distilled water were used to prepare the standard solutions. All solutions were stored in polyethylene containers. The containers were leached with 6 M nitric acid and rinsed thoroughly with demineralized-distilled water before using.

Each blank was prepared by adding to a volumetric flask (10, 25 or 50 ml) the same amount of HNO_3 as used for digestion, a volume of demineralized-distilled water equal to that of the digested sample and diluting to the mark with the appropriate electrolyte system.

QUALITATIVE APPROACH

The blank was transferred to the electrolysis cell and was purged for 5 minutes with nitrogen. The nitrogen stream was then diverted over the solution by turning the stopcock to the appropriate position on the sparge tube. A deposition potential was selected and the mercury drop was adjusted to give a size that corresponded to 3 divisions/drop on the micrometer head of the [illegible]. Stirring was initiated. The instrument was switched to "Cell" concurrently to activating a timing device. Thirty (30) seconds were allowed to pass after stirring was terminated, and stripping was initiated at 10 mv/s. Preconcentration and stripping were repeated to check for reproducibility. An aliquot of a standard solution of a metal ion (if [illegible]) of 30 seconds to 1 minutes were used and a blank volume of 25 ml was in the cell, 30 - 50 of 10 - 20 ppb of standard) was added to the cell and the solution was purged again. Stirring preconcentration, and stripping were conducted under the same conditions, and the spiked curve was obtained. Other metals were added sequentially and DPASV was conducted to assess their detectability in the blank and in the presence of potentially interfering analytes.

QUANTITATIVE APPROACH

Once an assessment was made to identify the metals that were detectable in a particular electrolyte system, the pH and ionic strength of that system were varied separately to ascertain conditions for optimizing the current-potential signal. A modified blank was prepared and the linearity between Ip and C, was investigated for each metal. Considerable time was saved by preparing a combined standard (composed of all of the detectable metals). Preconcentration and stripping were performed following each addition of standard.

The following are methods that were developed through this study.

ANALYTICAL METHOD NO. 1

SIMULTANEOUS IDENTIFICATION AND DETERMINATION OF ZINC, CADMIUM, LEAD, BISMUTH, AND COPPER IN EFFLUENTS

Analytes: Zn, Cd, Pb, Bi, and Cu — Matrix: Industrial or Domestic Effluent

Electrolyte System: Acetate buffer, pH=5.5-5.8
E_d = -1.4 V

Range:			
	Zn	0.5 —	115 ng/ml
	Cd	0.00 —	100 ng/ml
	Pb	0.10 —	200 ng/ml
	Bi	0.30 —	310 ng/ml
	Cu	0.50 —	118 ng/ml

Precision: (% relative standard deviation)					
	Zn	± 2.7	Cu	± 2.0	
	Cd	± 2.9	Bi	± 2.5	
	Pb	± 2.4			

Accuracy:		
	Zn and Cd	100 ± 6%
	Pb	100 ± 4%
	Bi and Cu	100 ± 6%

1. Procedure

1.1 Leach all glassware in 6N HNO_3 for 5 hours and rinse thoroughly with demineralized - distilled water.

1.2 Transfer digested sample from Teflon cup to a 25 ml volumetric flask. Add the appropriate amount of sodium acetate to acid solution to form a buffer of pH = 5.5 to 5.8. If the acid concentration is high in the digested sample, increase the concentration of sodium acetate or evaporate the solution slowly to drive off most of the acid and take up digestate in sodium acetate. Adjust pH to 5.5 - 5.8.

1.3 Transfer the solution to the cell and purge for 5 minutes.

1.4 Set the E_d to = 1.4 V. Divert the stream of nitrogen over the solution.

1.5 Stir solution and preconcentrate for 30 seconds to 5 minutes.

1.6 Turn off stirrer and allow 30 seconds for quiescent conditions to develop.

1.7 Initiate scan at 10 mv/s and scan to the desired potential of termination.

1.8 Repeat steps 1.4 - 1.7.

1.9 Spike with resp 10 - 100 of concentrated standard. Try to use a spike size that will give signals that are about twice the size of the original signals. (Step 1.9 is not necessary if a calibration curve is used).

1.10 Purge and repeat steps 1.4 - 1.7.

2. Calculation

$$C = i_1 v C_s / (i_2 v + (i_2 - i_1) V)$$

Where C_1 = original cell concentration
C_s = concentration of standard solution used for spiking
i_1 = peak height in original cell solution.
i_2 = spiked peak height
v = volume of standard solution added as spike
V = original sample volume

3. Interferences

In interferes with Cd and Tl interferes with Pb. Long preconcentration times and high concentration of analytes may cause a Cu - Zn intermetallic to form. This intermetallic strips at the same potential as that of Cu and enhances the Cu signal while lowering the Zn signal. It may be eliminated by using a shorter preconcentration time or diluting the sample solution.

ANALYTICAL METHOD NO. 3
SIMULTANEOUS IDENTIFICATION AND DETERMINATION OF ZINC, INDIUM, THALLIUM, BISMUTH AND COPPER IN EFFLUENTS

Analytes: Zn, In, Tl, Bi, and Cu

Matrix: Industrial or Domestic Effluent

Electrolyte System: Acetate buffer, pH=5.5-5.8
E_d^{p} =1.4 V

Range: Zn, Bi and Cu (same as Method 1)
In 0.3 ng/ml --- 100 ng/ml
Tl 0.10 ng/ml -- 300 ng/ml

Precision: Zn, Bi and Cu (same as Method 1)
(% Relative
Standard Deviation) In ± 5.0 Tl ± 2.6

Accuracy: 90 ± 6%

1. Procedure
   (Same as Method 1)

2. Calculations
   (Same as Method 1)

3. Interferences
   Cd interferes with In and Pb interferes with Tl.
   (See Method 1)

ANALYTICAL METHOD NO. 3
DETERMINATION OF LEAD AND THALLIUM IN EFFLUENTS

Analytes: Pb and Tl

Matrix: Industrial or Domestic Effluent

Electrolyte System: Acetate buffer, pH 5.0 - 5.8,
for total Pb plus Tl.
Add 0.80 g of EDTA salt
for Tl determination in the presence of Pb.

E_d = -0.8 V

Range: Pb 0.10 --- 200 ng/ml
Pt 0.10 --- 200 ng/ml

Precision (% Relative Standard Deviation): Pb ± 3.4
Tl ± 2.6

Accuracy: 95 ± 6%

1. Procedure:

Follow procedure in Method 1 to determine the sum of Pb and Tl in acetate buffer. Add EDTA salt and repeat the procedure to determine the amount of Tl present.

2. Calculations:

Subtract the concentration of Tl from the sum of the concentration of Tl and Pb.

3. Interferences:

There are no known interferences.

ANALYTICAL METHOD NO. 4
IDENTIFICATION AND DETERMINATION OF INDIUM IN EFFLUENTS

Analyte: In

Matrix: Industrial or Domestic Effluent

Electrolyte System: 0.1 NH_4ClO_4/NH - 0.015 M $C_6H_8O_7$ (pyroquallic acid)

E_d = -0.8

Range: 0.05 ng/ml --- 170 ng/ml

Precision (% Relative Standard Deviation): ± 2.7

1. Procedure

(Same general procedure for DPASV)

2. Interferences

(There are no known interferences.

ANALYTICAL METHOD NO. 5
DETERMINATION OF TIN IN EFFLUENTS

Analyte: Sn

Matrix: Industrial
or Domestic Effluent

Electrolyte System: 5N HCl

E_d =-0.8 V

Range: 0.5 ——— 100 ng/ml

Precision: ± 3.8
(% Relative
Standard Deviation)

Accuracy: Undetermined (low level blank was difficult to obtain)

1. Procedure

Digest sample according to the Parr bomb digestion procedure. Carefully evaporate sample to near dryness, without heating too rapidly. Take up the digestate in 5N HCl.

2. Calculations

(Same as Method No. 1)

3. Interferences

Pb interferes with the determination of Sn.

ANALYTICAL METHOD NO. 6
DETERMINATION OF ANTIMONY IN EFFLUENTS

Analyte: Sb

Matrix: Industrial
or Domestic Effluent

Electrolyte System: 1M H Cl

E_d =-0.8 V

Range: 1 ----- [illegible]/ug/ml

Precision: ± 4.2
(% Relative
Standard Deviation)

Accuracy: Undetermined (low level blank was difficult to obtain)

---

1. Procedure

Same as Method No. 5 except the digestion is to be taken up in [illegible]

2. Calculations

(Same as Method 1)

3. Interferences

No apparent interferences

ANALYTICAL [illegible] NO. 7
DETERMINATION OF NICKEL IN EFFLUENTS

Analyte: Ni

Matrix: Industrial
or Domestic Effluent

Electrolyte System: ammonia-tartrate

E_d =-1.0 V

Range: 0.8 --- [illegible]mg/ml

Precision: ± 4.0
(% Relative
Standard Deviation)

Accuracy: 0% ± 0%

---

1. Procedure

Same as Method No. 5 except the digestate is taken up in [illegible] ammonia - .2M tartrate.

2. Calculations

Same as Method No. 1

DETECTION LIMITS AND PRECISION

The operational definition of detection limit used by the investigator was the minimum detectable amount of analyte that produces a signal significantly different from zero.

A large number (n>10) of blanks were analyzed and the standard deviation for each element present was calculated. The detection limit in each case was calculated as

$$D.L. > t\,\beta_b \sqrt{\frac{1}{n_s} + \frac{1}{n_b}}$$

Where n_s and n_b were the number of determinations performed on the sample and blank, respectively. The parameter t was taken from the t - distribution table (3), its value depended upon the degrees of freedom $n_s + n_b - 2$ at the 99% probability level.

Precision data were acquired by analyzing a large number (n > 10) of samples of the same effluent and determining the % relative standard deviation. Since the method of standard additions were used to acquire quantitative data the reproducibility was the same as the precision. Typical reproducibility data are shown in Figure 2.

DEPENDENCY OF PEAK CURRENT ON CONCENTRATION

Calibration curves are prepared from peak-current versus concentration data. Figure 3 gives a set of typical calibration curves. These were determined while simultaneously stripping Zn, Cd, Pb, Cu and Bi in acetate buffer. The method of standard additions gave results that were not significantly different from results acquired by use of the calibration curves. Of course, use of the standard additions method required that there is a linear relationship between i_p and C. In the application of these methods the calibration data were treated by the method of least squares.

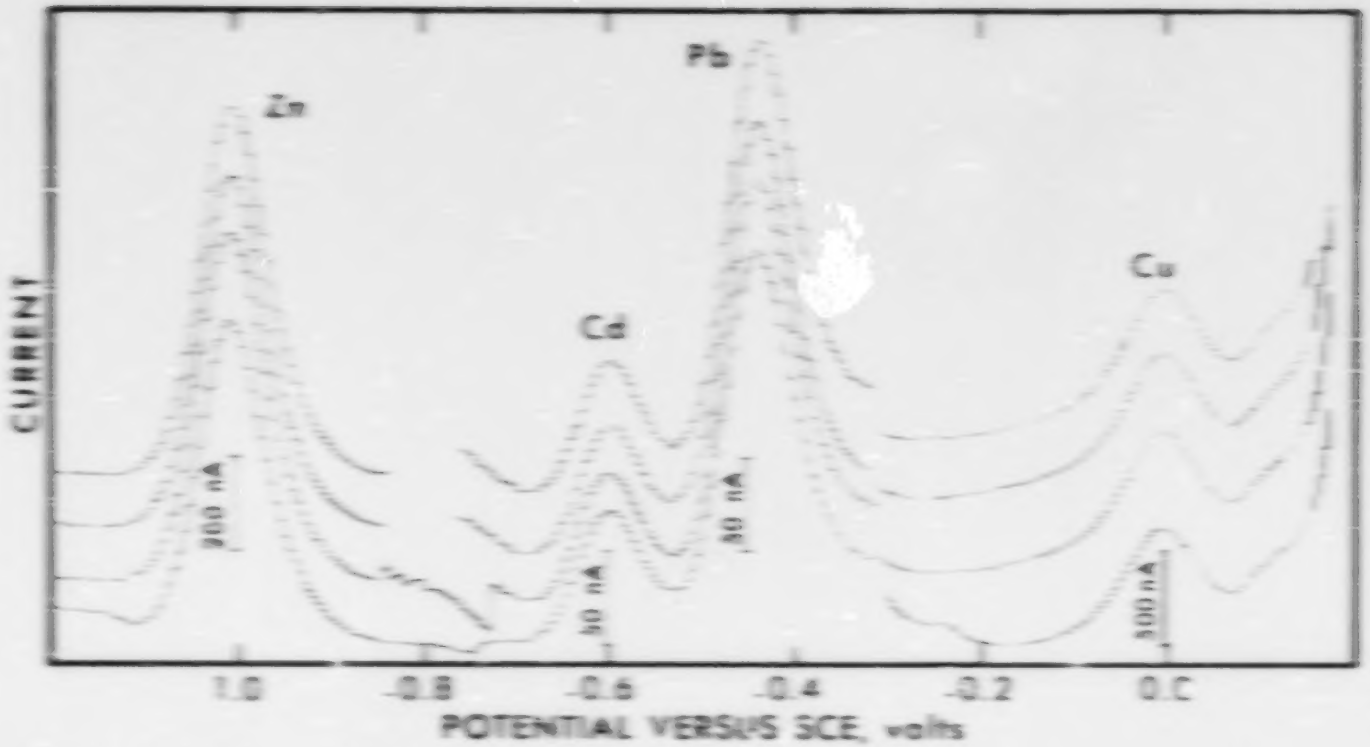


Figure 2. Reproducibility of DPASV for simultaneous stripping of zinc, cadmium, lead, and copper in 0.5F sodium fluoride.

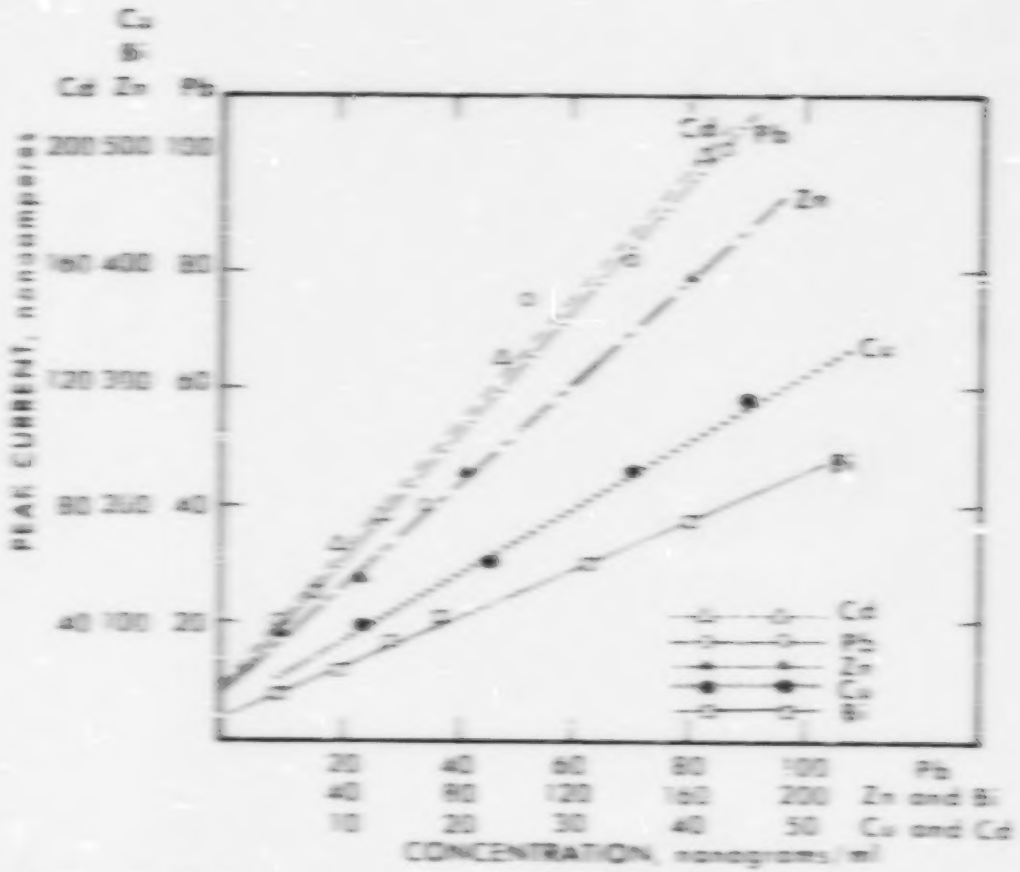


Figure 3. Peak current versus concentration for the simultaneous stripping of Zn, Cd, Pb, Bi and Cu. [Acetate buffer of pH 5.48, t_d^0=30 S, E_d= -1.400V, m.S = 3]

SECTION VII

EVALUATION AND APPLICATION OF ANALYTICAL METHODS

The methods have been applied to the identification and determination of trace metals in a variety of effluents. The various types and the number of samples studied in this laboratory are listed in Table 2. This represents a broad spectrum of effluent matrices that were tested, and the conclusions presented in the first part of this report are derived from a comprehensive matrix data base.

A mixture constituting various amounts of practically all types of effluents listed in Table 2 was developed and analyzed. The results along with precision data are given in Table 3.

A second mixture composed of effluents and tap water was developed and analyzed. The results along with the recovery data are shown in Table 4. This recovery reflects the total efficiency for the digestion procedure, sample transfer, and analytical measurement. Since it was acquired by the use of a real sample of perhaps the most complex matrix available, it is a good representation of the applicability of the entire procedure for DPASV, provided careful analytical work is conducted.

Table 5 contains a listing of some results that were obtained for some of the different effluent types. The Egg Processing and Steel Mill sample required the greatest amount of time for digestion (10 hours).

TABLE 2. TYPES OF EFFLUENTS AND NUMBER OF SAMPLES ANALYZED THROUGH THIS STUDY

Effluent Type	Further description	No. of Samples Studied
Textile & domestic	Waste from corrugated iron manufacturing facility also. Influent to oxidation pond.	6
Raw sewage	Domestic waste.	10
Printing industry and domestic waste	60% industrial and 40% domestic. Raw waste.	5
Meat Packing	Different locations.	3
Aluminum products	Collected from pond-after oil separation.	6
Aluminum products	Raw. After pH adjustment.	3
Paper mill	Raw waste.	5
Paper mill	Effluent from clarifier.	3
Egg treatment	Raw waste.	3
Steel mill	Raw waste.	35
Steel mill	Refined.	18
Textile	Raw.	10
Slaughter house	Raw.	3
Metals plating	Raw.	6
Metals plating	Refined.	3
Soft drink	Raw.	3
Synthetic Fibers	Raw.	3
Dyeing and Finishing	Raw.	1
Chicken Farm	Raw	3

TABLE 3 TRACE METALS IN A MIXTURE OF INDUSTRIAL EFFLUENTS AND PRECISION DATA

Element	Concentration, µg/ml				Standard Deviation µg/ml
	Sample #1	Sample #2	Sample #3	Sample #4	
Zn	17.2	21.0	21.8	33.4*	± 2.00
Cd	20.4	20.4	20.0	18.3	± 1.33
Pb	27.4	27.0	30.1	27.2	± 0.85
Bi	14.50	4.01	4.38	4.13	± 0.18
Cu	12.0	13.0	12.4	12.7	± 0.68

* Apparent contamination. Rejected this datum in computing the standard deviation.

TABLE 4. RECOVERY DATA FOR THE SIMULTANEOUS DETERMINATION OF ZINC, CADMIUM AND LEAD IN INDUSTRIAL MIXTURE II

Element	Naturally Occurring (µg/ml)	Added (µg/ml)	Found (µg/ml)	Recovery (%)
Zn	15.4	4.44	19.0	113.0
	20.1	4.02	20.5	95.1
Cd	4.43	4.35	8.63	97.5
	6.70	5.34	11.65	108
Pb	8.34	3.54	11.4	105
	8.05	4.01	14.0	101.8

TABLE 6. RESULTS FROM APPLICATION OF DRAV TO A VARIETY OF EFFLUENTS

Effluent Type	Concentration, mg/ml				
	Zn	Cd	Pb	Cu	Hg
Textile	0.00	11.0	16.9	34.1	3.72
Printing	2.30	1.5	7.8	----	----
Lake Marion	30.01	----	121	2.43	----
Egg Processing	308	114	83.4	101	----
Steel Mill	848	10.3	711	420	11
	$X10^3$	$X10^3$	$X10^3$	$X10^3$	$X10^3$

SECTION VIII

COMPARISON OF DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY AND FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY FOR EFFLUENT ANALYSIS

Flame atomic absorption spectrophotometric data on metals in effluents were acquired by using a Model 503 Atomic Absorption Spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut). For most samples a triple slot burner head was used and the deuterium arc background corrector was activated. New single element hollow cathode lamps of short shelf life were used in all cases except for the determination of copper. This element was determined while using a Cr - Cu - Fe - Mn - Mo multielement lamp. An air - acetylene flame was employed for all samples and final readout data were acquired while operating in the concentration mode with integration times of 3 and 10 seconds.

Refrigerated samples were allowed to reach thermal equilibrium with the laboratory atmosphere prior to analysis. Effluents that were difficult to aspirate because of a large percentage of particulates were filtered. No sample pretreatment was conducted with exception of the addition of nitric acid (approximately 5 ml of 1:1 v/v/ liter of effluent) immediately following sample collection for the purpose of preservation. Figures 4 and 5 are typical calibration curves obtained by flame AAS. In most cases linearity complied with the specifications given in reference (3).

Table 6 contains some of the quantitative data obtained from the comparative analyses of effluents by DPASV and flame AAS. The DPASV results were ascertained by employment of the methods developed through this study. The working solution that resulted after application of the Pure acid digestion bomb technique and dilution contained levels of metals that ranged from 10 ng/ml to 100 ng/ml.

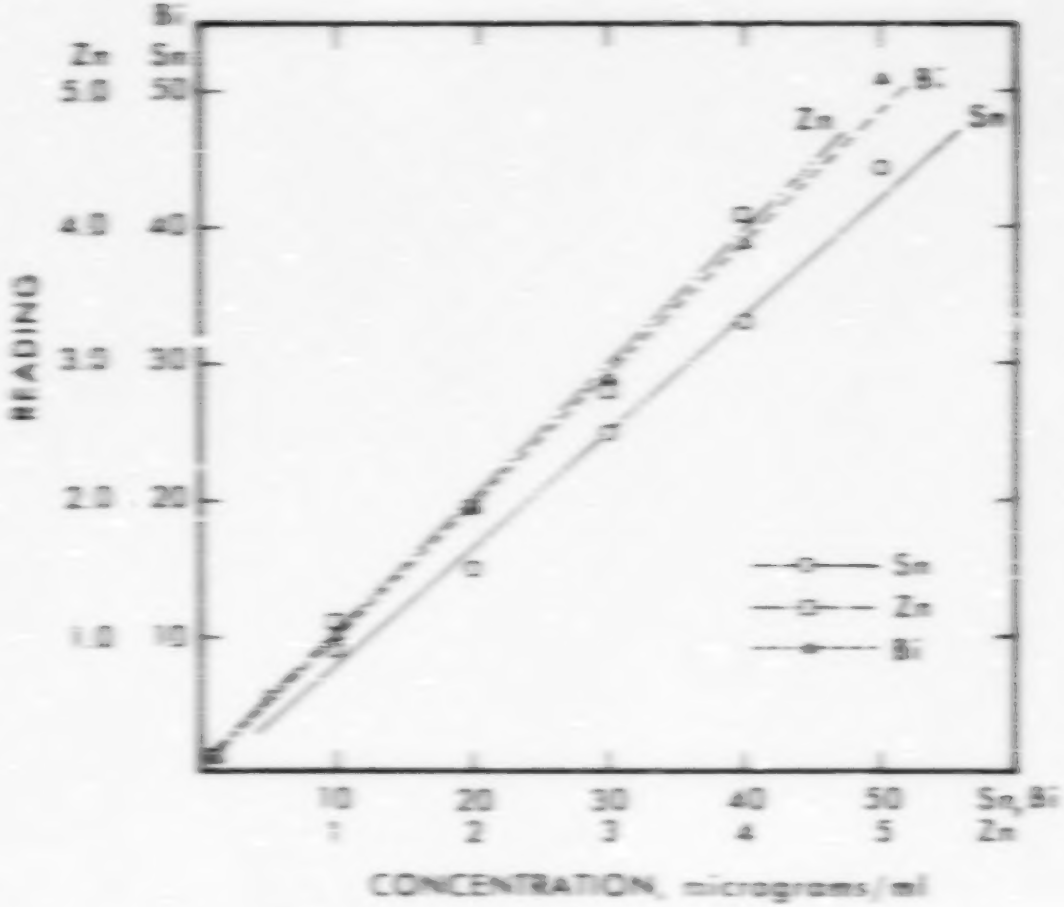


Figure 4. Atomic absorption calibration curves for tin, zinc, and bismuth.

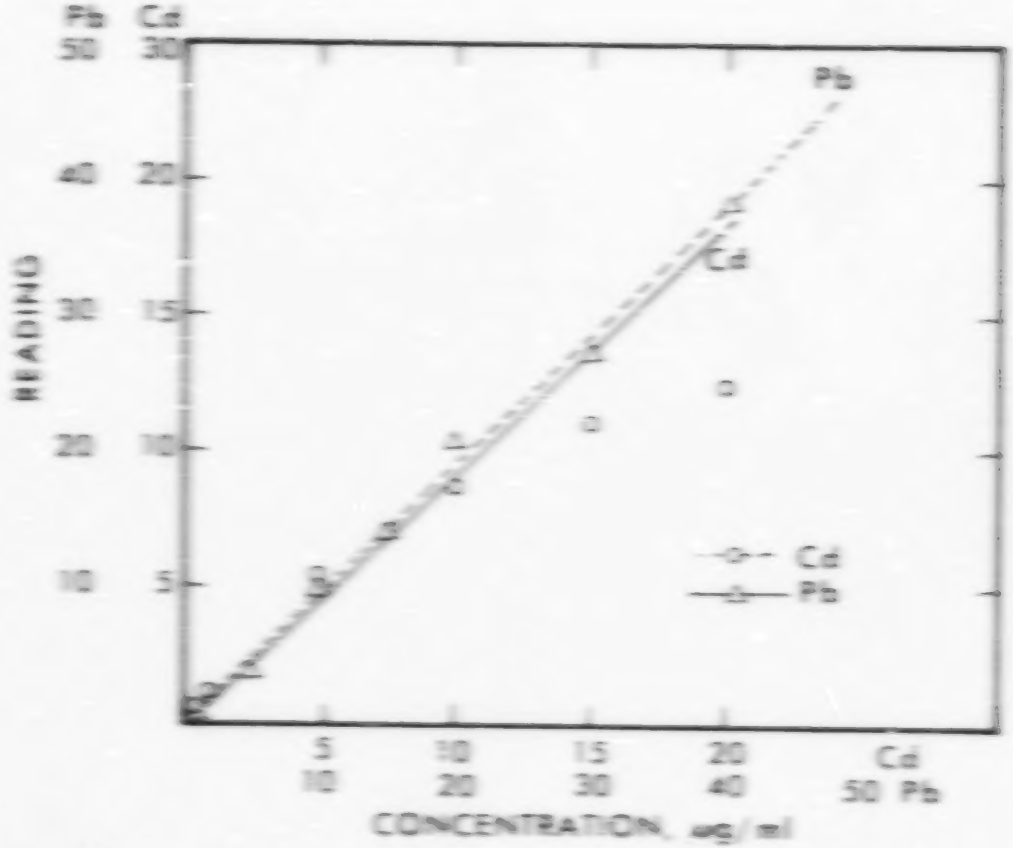


Figure 5. Atomic absorption calibration curves for cadmium and lead.

TABLE 6. COMPARISON OF DPASV AND FLAME AAS DATA FOR METALS IN EFFLUENTS

Sample no. and effluent type	Element	Concentration, (ug/ml) DPASV	AAS	Percent Difference
Mixed sample #19	Zinc	0.72	0.80	10
	Cadmium	30.6	30.9	1.4
	Lead	30.1	31.5	7.08
	Copper	16.3	17.3	9.90
	Bismuth	4.38	3.51	41.4
Steel Mill #4C38	Cadmium	.07	0.07	0
	Lead	5.97	5.30	15.9
	Copper	.054	0.07	13.8
	Bismuth	11.6	13.9	10.1

TABLE 7. COMPARISON OF SENSITIVITIES, DETECTION LIMITS AND LINEARITY RANGE OF TRACE METAL DETERMINATION FOR DPASV AND FLAME AAS

Element	Detection Limit DPASV* (ug/ml)	AAS (ug/ml)	Sensitivity DPASV (ug/ml/nA)	AAS (ug/ml/%abs)	Linearity Range DPASV* (ug/ml)	AAS (ug/ml)
Zn	0.5	3	5	18		1,000
Cd	0.08	5	1	85		3,000
Pb	0.10	80	3	500		30,000
Bi	0.38	50	8	400		3,000
Cu	0.50	5	4	80		5,000
Tl	0.10	300	3	600		30,000
In	0.30	50	3	250		50,000

The good agreement that exists between the results for most metals suggests that DPASV competes well with the present widely accepted technique, AAS, for metal determination. It was observed in most cases throughout this comparative study that the Parr bomb digestion - DPASV results were higher than the flame AAS data. The consistency in this trend together with the accuracy of the DPASV methods suggests that the Parr bomb digestion technique and the sensitivity of DPASV provide for the combined total determination of metals in the solution and particulate phases of an effluent sample.

The rather poor agreement between the results of the two techniques for bismuth in mixed sample #18 is apparently due to the fact that level of this metal is close to its lower detection limit for AAS. The accuracy of the DPASV method for Bi at the 100 - 200 ng/ml (the range of concentration of Bi in the working solution for which this sample was prepared).

Table 7 lists sensitivity, detection limits, and linearity (upper limit), data for both techniques. Table 8 lists the items that constitute start-up costs for each method. It appears that DPASV is superior to AAS in terms of detection limits, sensitivity, and cost (see Table 9). The precision for the two techniques is comparable.

TABLE 8. COMPARISON OF START-UP COSTS FOR DPASV AND FLAME AAS

Category	Estimated Cost ($) DPASV		AAS
Basic Instrumentation	6,000		10,000
Needed Accessories	1,750		1,400
DMDE Set Up six capillaries 4 cells and 3 leads		six lamps and burner head	
Reagents and supplies (start-up)	350		400
TOTAL	-----	fan and venting	100
	$7,300		$10,000

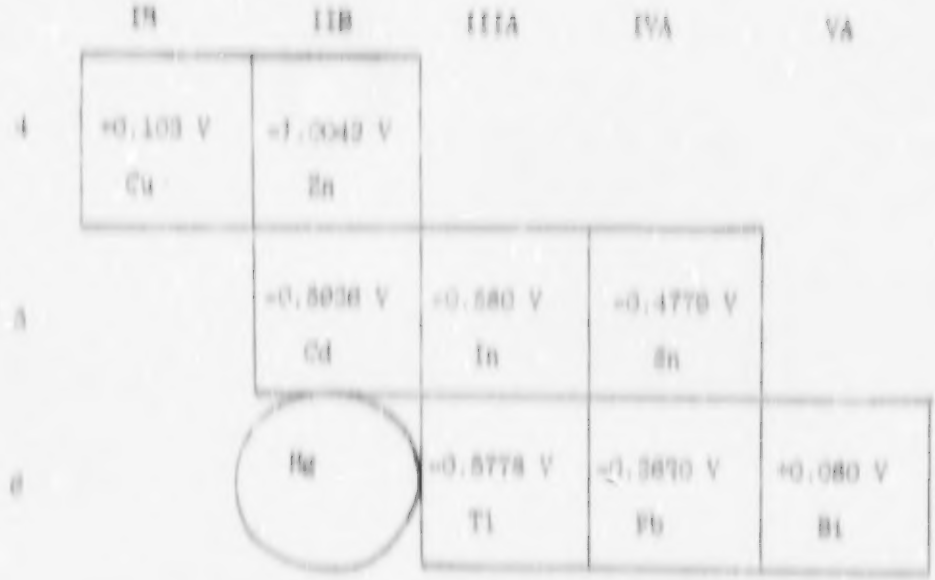
TABLE 9. ADVANTAGES AND DISADVANTAGES OF DPA/V AND FLAME AAS

Category	Advantages and Disadvantages DPA/V	AAS	Superior technique
1. Start-up costs	Estimated to be 1/2 about 2/5 the costs for AAS		DPA/V
2. Annual Maintenance	Have used instrument for 3 years at zero maintenance cost	$1,000 (routine)	DPA/V
3. Technical skill required	Highly sensitive experienced technician		AAS
4. Instrumental Tune-up	Immediate use	Must tune-up for optimum performance	DPA/V
5. Counter space	Very compact	Requires about 4 times the space for DPAS	DPAV
6. Supportive supplies and equipment			DPA/V
7. Sample preparation	Must digest completely	Little or none	DPA/V
8. Precision			Comparable
9. Accuracy			Comparable
10. Detection Limits	Depends on purity of reagents and preconcentration time		DPA/V
11. Sensitivity	Very sensitive		DPA/V

SECTION IX

DISCUSSION

DRAIN AND CHEMICAL PERIODICITY



A number of interesting correlations have been made between the DRAIN characteristics of these elements and their chemical periodicities. The number that is written above each element in the above portion of the periodic Table is the standard reduction potential (E) of the most stable form of the metal ion in aqueous acid media. For comparative purposes, these potentials are given in reference to the SCE.

Table IX gives the electronic configuration of each ion along with its reduction potential.

TABLE 10. CORRELATION BETWEEN REDUCTION POTENTIALS AND ELECTRONIC CONFIGURATIONS OF METAL IONS

Metal ion	Outer Electronic Configuration	Reduction potential
Cu^{+2}	$4s^2 4p^6 4d^9 5s^1$	+ 0.161
Bi^{+3}	$6s^2 5d^{10} 6p^3$	+ 0.080
Pb^{+2}	$6s^2 5d^{10} 6p^2$	- 0.1260
Sn^{+2}	$5s^2 4d^{10} 5p^2$	- 0.1375
Tl^{+1}	$6s^2 5d^{10} 6p^1$	- 0.3728
In^{+3}	$5s^2 4d^{10} 5p^1$	- 0.340
Cd^{+2}	$5s^2 4d^{10} 5p^0$	- 0.4030
Zn^{+2}	$4s^2 3d^{10} 4p^0$	- 1.0403

Since the reduction potential is related to the free energy change (spontaneity) for the corresponding half-cell reaction it may be looked upon as a quantity related to the energy necessary to produce the neutral atom or amalgam. Zn^{+2} requires the greatest amount of energy to be reduced, and this apparently is related to the scheme that two electrons must be placed in the somewhat shielded 4s empty orbital. Similarly, Cd^{+2} ion has all 4 d orbitals filled, shielding the 5s empty orbital, but the reduction potential for Cd^{+2} is over 400 mv more positive than the value for Zn^{+2} ion. The outer orbitals for Cd^{+2} are for principal levels 4 and 5 while those for Zn^{+2} are 3 and 4. This may account for the considerable difference in the reduction potentials of the two ions. The entire order of the reduction potentials of the metal ion can be explained based on their electronic configuration. Notice the order by which the ions occur in Table 10 and the order by which they exist in the periodic chart. When Cu^{+2} is excluded there appears an interesting correlation between the reduction potentials of these ions and their periodic placement.

Another interesting correlation was made between the electronic densities (4) of the neutral atoms and their stripping positions on the current-potential curves. A typical case is shown in Figure 6.

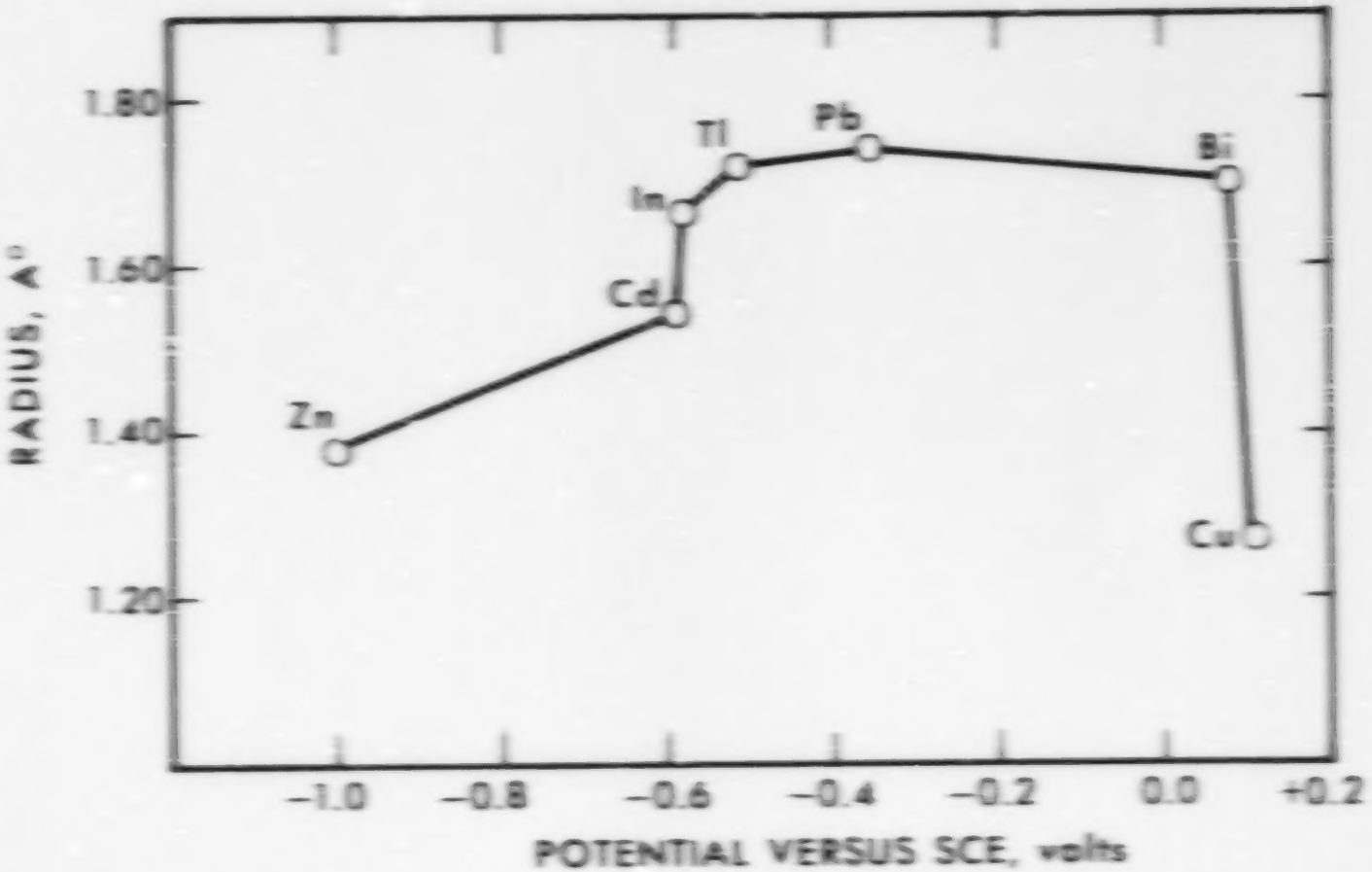


Figure 6. Dependency of reduction potential on atomic radius.

Separation of Bi and Cu

The sensitivity of the signal for Tl in acetate buffer is approximately twice that of the acetate buffer-EDTA solution, 2.42 nA/ng/ml and 1.35 nA/ng/ml, respectively, with the t_d = 10 seconds. The detection limits for Tl are 1.25 ng/ml and 1.58 ng/ml for acetate buffer and acetate buffer - EDTA solution, respectively with a t_d = 10 seconds. The $E_{p/2}$ value for Pb + Tl in acetate buffer is -0.506 V versus SCE while a value of -0.550 V versus SCE exists for Tl in acetate buffer - EDTA solution.

Through a separate study performed in this laboratory, it has been determined that the diffusion coefficient of Tl^{+1} is twice that of Pb^{+2}. Tl^{+1} gives virtually the same i_p/C value (6.22 x 10^{+1} nA/M) as Pb^{+2} (6.28 x 10^{+1} nA/M) when run separately in acetate buffer. Thus in acetate buffer, the amount of electricity or total charge (coulombs) involved in the stripping of a certain concentration of Tl^{+1} should be the same as the one for Pb^{+2} under the same experimental conditions. In the determination of the sum of the concentrations for Tl and Pb (which have the same $E_{p/2}$ it does not matter which of the two metal ion standards is used for the spike.

EDTA completely complexes the lead to form a stable species when it is added to the acetate buffer system. Tl gives a good signal in the presence of EDTA and can be readily determined in this new medium.

Separation of Bi and Cu

A number of workers have experienced difficulty in determining bismuth in the presence of copper. Figure 7 shows how acetate is used to separate the signals for bismuth and copper. Greater consistency in the data was obtained when the decaying portion of the wave was used to determine i_p for copper.

A different electrolyte system that provides for the simultaneous determination of Bi and copper is 0.1 M NH_4Cl - 0.2 M $(NH_4)_2CO_3$.

Ammonium chloride and potassium carbonate separately do not lead to the separation of Cu and Bi. Figure 8 reveals how the combination of the two effect the needed separation. Curves A and B represent the stripping for a nonpurged and purged solution - in 0.1 M NH_4Cl. Curve C is obtained after traces of Pb, Cd and Cu have been added. Curve D was run after the NH_4Cl solution was made 0.2 F in K_2CO_3. The addition of carbonate ion causes all species to be stripped at more negative potentials. Peaks 1 and 2 in curve C become 1 and 2, respectively, in curve D while 3 splits into two peaks. Curve E is a repeat run, and the reproducibility is very good. Lead and copper standards were added before running curve F and we can see that Cu is component C_1 while Cu is Bi, just the reverse order as occurs in acetate. Notice that the front part of the wave for Bi has decreased since the addition of Cu. This forces one to read the decaying current for Bi, which gives good reproducibility, even when the solution is spiked with copper.

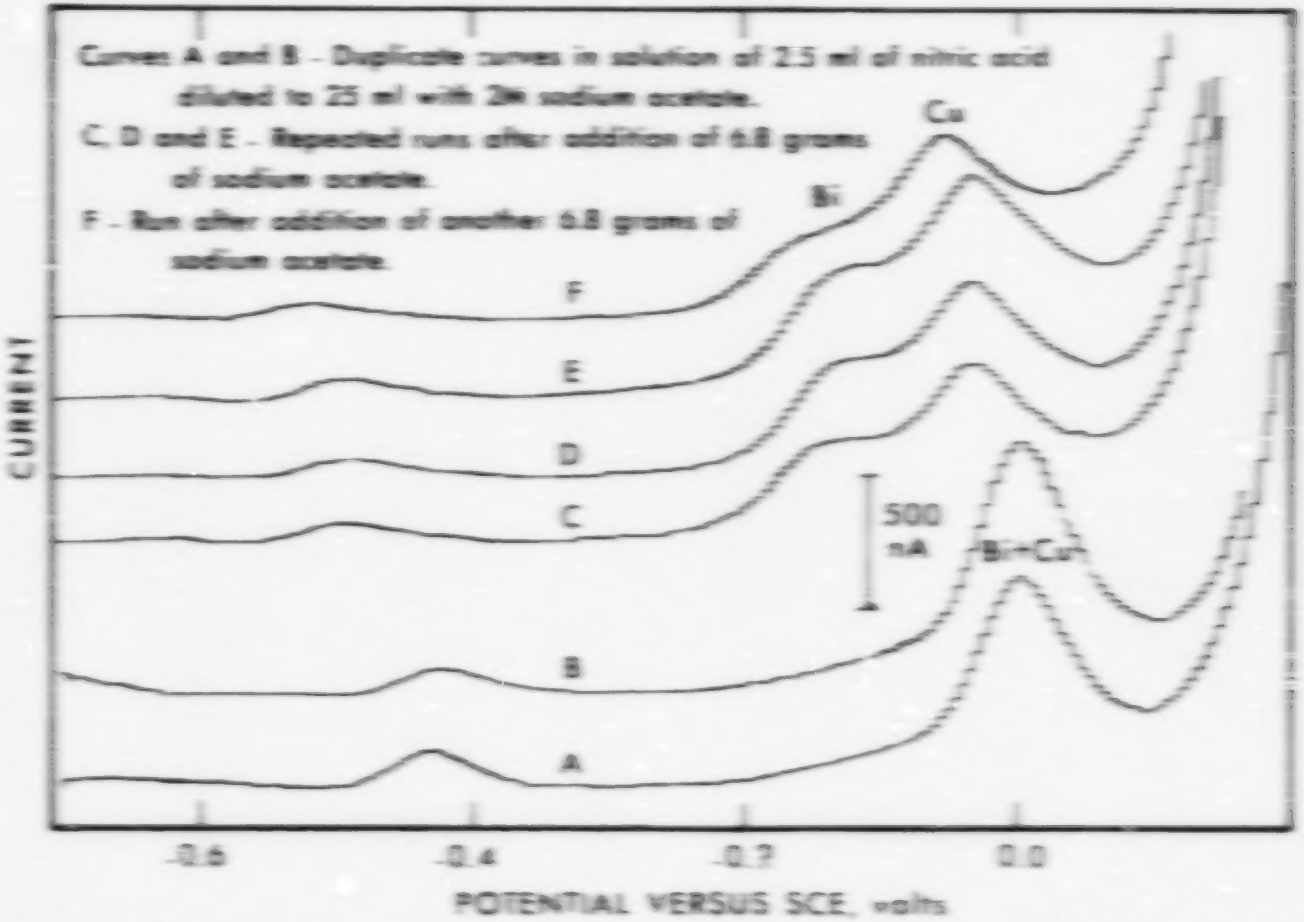


Figure 7. Separation of copper and bismuth signals for DPASV using acetate ion.

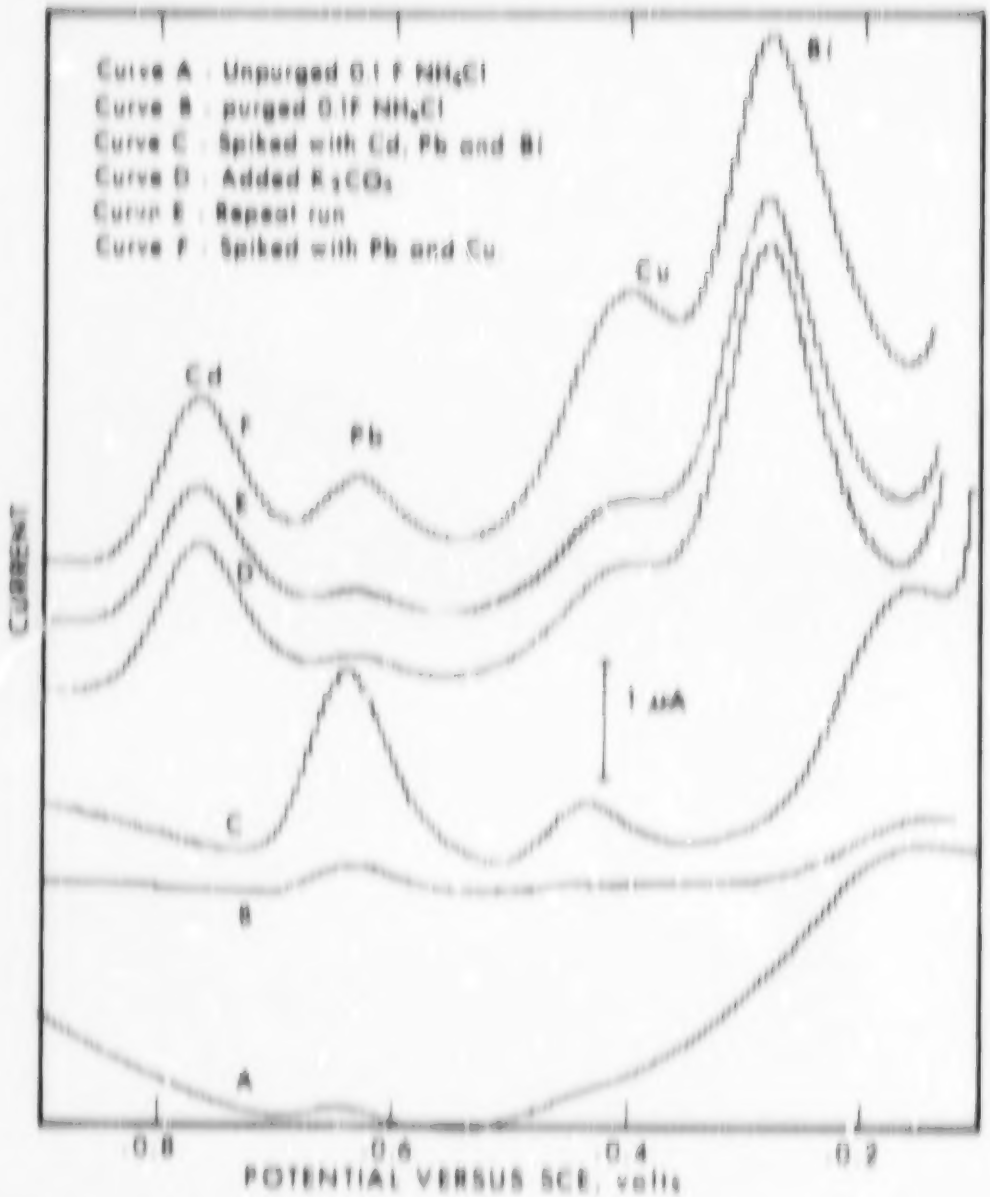


Figure 8 Current potential curves for simultaneous stripping of Cd, Pb, Cu and Bi in the presence of ammonia and acetate

Summary - The technique of DPASV is highly sensitive and requires an experienced analyst to apply the associated methods for determining a number of metals. The investigation has attempted to focus on those elements that are relatively ubiquitous, difficult to determine by other methods, are known toxicants or have questionable toxicity, and are likely to be more prevalent in effluents than other metals. Although through this investigation elements such as antimony, tin, and nickel have been explored using a number of electrolyte systems, this report does not preclude the extension of this list of metals to a wider spectrum.

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